

Infrared Spectra of High Pressure Carbon Monoxide

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INFRARED SPECTRA OF HIGH PRESSURE CARBON MONOXIDE

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We report infrared (IR) spectroscopic measurements of carbon monoxide (CO) at high pressures. Although CO is one of the simplest heteronuclear diatomic molecules, it displays surprisingly complex behavior at high pressures and has been the subject of several studies [1-5]. IR spectroscopic studies of high pressures phases of CO provide data complementing results from previous studies and elucidating the nature of these phases. Though a well-known and widely utilized diagnostic of molecular systems, IR spectroscopy presents several experimental challenges to high pressure diamond anvil cell research. We present measurements of the IR absorption bands of CO at high pressures and experimentally illustrate the crucial importance of accurate normalization of IR spectra specially within regions of strong absorptions in diamond.

Keywords: Carbon Monoxide; High Pressure; Diamond Anvil Cell; Sapphire; Infrared Spectroscopy.

1. INTRODUCTION

High pressure phase transformations of carbon monoxide (CO) have been the subject of several recent experimental and theoretical studies [1,5]. Such works have been motivated by several important scientific considerations, from furthering the fundamental understanding of properties and phase transitions in simple heteronuclear diatomic molecular solids to the technological utilization of CO in industrial applications [6]. CO is also a common high explosive detonation product, and scientific data on its high pressure properties are vital to developing and validating computational models of explosive processes [7].

The phase diagram of CO has been studied over a modest range of pressures and temperatures [2-4]. At room temperature, CO is a fluid up to 2.5 GPa, where it freezes into a disordered hexagonal phase (space group $P6_3/mmc$, β -phase). At still higher pressure, ~ 5.2 GPa, CO undergoes a structural transformation to a disordered cubic phase (space group $Pm\bar{3}n$, δ -phase) [3]. In previous work [1-2] for pressures above ~ 5 GPa, CO was transformed irreversibly into a dark red substance upon exposure to high intensity argon ion laser light. We characterized the infrared (IR) absorption of this material under pressure and identified several candidate species [1] consistent with the measured spectra including a polymer with a vinyl-ester like monomer unit of $[-(C=O)-O-(C-)=C<]$.

Several questions remain unanswered about the bonding nature of both high pressure molecular CO as well as the high pressure CO-derived phases. Specifically, key bonding information falls within the frequency regime of the IR absorption bands in diamond and thus has proven to be experimentally difficult or impossible to extract. The standard diamond anvil cell (DAC) is hampered by IR absorption bands of the anvils between ~ 1000 to 4000 cm^{-1} . The position, strength, and width of the diamond absorption bands exhibit a sensitive dependence on impurity concentrations, temperature and pressure[8-

10]. Previous IR studies of DAC samples have corrected for such behavior [11,12], but special care and control measurements were necessary. In contrast, sapphire anvil cells (SAC), though limited to lower pressures, present an open optical window free of obscuring absorption features from 1500-50,000 cm^{-1} . In this study we have collected IR spectra of CO at high pressure with the goal of more precisely determining the bonding states. We compare measurements obtained through the DAC and SAC approaches and demonstrate the challenges of conclusively identifying IR absorption features of even moderate strength in a DAC within the spectral regions below 2500 cm^{-1} .

2. EXPERIMENTAL APPROACH AND RESULTS

The CO samples were prepared and loaded using standard high pressure techniques described previously [1]. We utilized both diamond (type Ia) and sapphire anvils with $\sim 250\ \mu\text{m}$ diameter flat tips and tip-to-base distances of approximately 1.3 mm mounted in Merrill-Bassett cells. We prepared CO samples with a purity exceeding 99.99% and dimensions of $\sim 175\ \mu\text{m}$ diameter and $\sim 30\ \mu\text{m}$ thickness. The pressures were measured using the ruby fluorescence technique, and IR spectra were collected using a commercial FTIR spectrometer.

Representative IR spectra measured at room temperature of CO samples in diamond and sapphire anvil cells at pressures of $\sim 1.0\ \text{GPa}$ and $20\ \text{GPa}$ are shown in Fig. 1. These spectra have been normalized to the transmission spectrum of an empty pressure cell. The fluid phase of CO at $1.0\ \text{GPa}$ was clear, whereas the sample at $20\ \text{GPa}$ was yellow, gradually darkening with time, possibly similar to the behavior of CO samples above $\sim 5\ \text{GPa}$ observed by Katz *et al.* [3]. We still observed laser induced photoreaction in the sample at $20\ \text{GPa}$ even with the lowest laser powers (at 514.5nm).

3. DISCUSSION AND CONCLUSIONS

The IR spectra of the DAC samples are clearly complicated by the absorptions in the diamond anvils. For our geometry, transmissions through the bands at $\sim 1000\text{-}1200\ \text{cm}^{-1}$, $1800\text{-}2200\ \text{cm}^{-1}$ and $2500\text{-}2700\ \text{cm}^{-1}$ bands were approximately 10^{-3} , 10^{-3} , and 10^{-2} , respectively. In the fluid phase one expects absorption bands due to the single molecule interactions, i.e., a continuation of the gas phase IR vibrational frequency of the CO molecule near $2143.2\ \text{cm}^{-1}$. Consistent with this expectation, we observe a band in the fluid phase DAC sample ($P=0.95\ \text{GPa}$) at $2145\ \text{cm}^{-1}$ as indicated by the dagger in Fig. 1a. However, we found normalization of spectra within the proximity of strong diamond absorption regions (Fig. 1a and 1b) unreliable and increasingly structured with changing pressure. Thus, we deemed the conclusive identification of modes within the vicinity of these bands to be tentative.

In order to address these difficulties, we utilized the SAC to attempt to resolve these questions. In stark contrast to the DAC samples, the IR spectrum of the CO in a SAC (Fig. 1c) is easily interpretable. Comparing the fluid phase CO spectra in the DAC and SAC, we conclude that a feature at $2333\ \text{cm}^{-1}$ (asterisk) in the DAC sample is not derived from the CO sample. This feature originates from a shift in the diamond anvil's IR absorption relative to the zero pressure empty cell reference and illustrates the difficulty inherent in normalizing the DAC sample. The features at 2145 and $4255\ \text{cm}^{-1}$ are confirmed. The former feature is saturated in the SAC, and several sharp satellite peaks appear on its low energy side. The latter feature at $4255\ \text{cm}^{-1}$ is present in the both sample, but much weaker in the DAC sample.

because the SAC sample is thicker and thus more optically dense. The significant differences observed between the low pressure CO sample in a SAC versus a DAC suggest that the IR spectrum of the 20 GPa DAC CO sample must be treated with reservations and further measurements using a SAC are crucial to making definitive identifications of the IR spectral character.

IR absorption features are sensitive probes of the bonding character of high pressure phases. Intrinsic absorption features of diamond present significant challenges to the interpretation of the IR spectra of samples contained in a DAC. Often times, the approach of normalizing measurements taken at high pressures are normalized to measurements taken at lower pressures, in order to minimize changes in samples size, thicknesses, as well as absorptivity changes in the anvils. This approach is not satisfactory when dramatic absorptive changes occur in samples (or for that matter also in the anvils) with succeeding pressures, as is the case in our CO samples at 5 GPa and higher. The SAC, while limited to pressures of only a few tens of GPa, permits the collection of dramatically cleaner spectra with no ambiguity in the identification of absorption lines. Beyond the work discussed here, these data point out the possibility of false spectral features caused by the difficulty of normalizing DAC IR spectra and the need for caution when identifying IR absorption features in DACs near the intrinsic diamond absorption bands. Alternatively, type IIa diamonds have fewer intrinsic IR absorption bands, but such diamonds still have some strong IR features and the additional expense of such anvils limits their use. In summary, we expect that further work using sapphire anvils over their range of accessible pressures will permit a thorough study of the IR modes in CO and their implications for the high pressure phases of CO. This work was performed under the auspices of the U.S Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

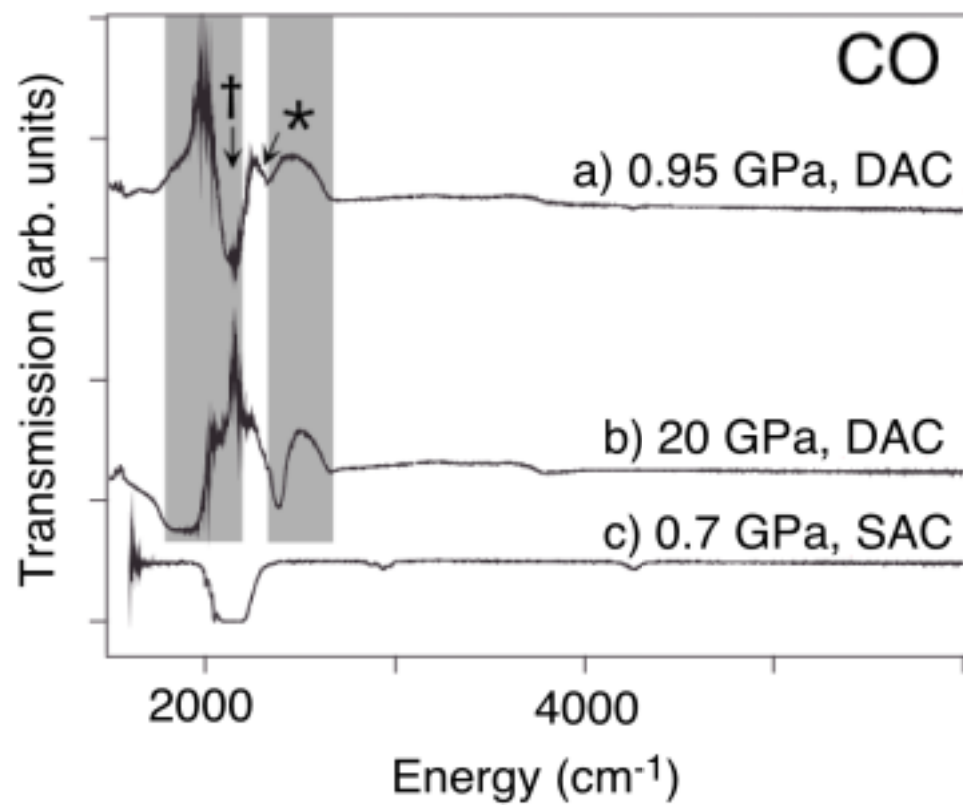
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Figure Captions

FIGURE 1. Comparison of IR spectra of high pressure CO in a DAC (a and b) and SAC (c). Spectra are normalized to spectra of empty high pressure anvil cells. Shaded regions indicate regions of strong diamond absorption. SAC and DAC traces are terminated in regions where the anvils are opaque. The triplet in the sapphire spectrum at 2900 cm^{-1} is a contaminant on one of the optical surfaces external to the sample. Curves are displaced vertically for clarity. Symbols: see text.



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FIGURE 1

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